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Preparation and photoelectrochemical applications of chemically synthesized Sb-doped p-AgIn₅S₈ film electrodes

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ABSTRACT

Chemically synthesized Sb-doped p-type AgIn₅S₈ films with several parameters, such as ratios of Sb/Ag in the reaction solution and multiple depositions of films, were grown on indium–tin–oxide coated glass substrates in this study. The X-ray diffraction patterns of samples show the cubic AgIn₅S₈ phase in these films. The thicknesses, energy band gaps, and carrier densities of these samples were in the ranges of 537–776 nm, 1.71–1.73 eV, and 6.57×10^{14} – 8.82×10^{14} cm⁻³, respectively. The maximum photocurrent density of samples with an external potential of –3.5 V vs. a Pt electrode was found to be –5.02 mA/cm² under illumination using a 300 W Xe lamp system.

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1. Introduction

Generating storable chemical fuels using renewable energy has become an important development field because of the increasing demand for energy. One way of achieving this is water splitting using a photoelectrochemical (PEC) system. PEC systems have been well-studied since Fujishima and Honda proposed the process of photosplitting of water in 1972 with an n-type TiO₂ electrode [1]. However, the performance of a PEC system using an n-TiO₂ electrode is limited to ultraviolet light, which entails 5% of the photons of the AM (Air Mass) 1.5 solar spectrum [2]. Low solar absorption by TiO₂ is due to its large band gap of 3.0–3.2 eV, which can only absorb light of wavelengths shorter than 388–413 nm. To improve the PEC performance of water splitting,

various new visible-light active photocatalysts have been developed. Among these visible-light active photocatalysts, I–III–VI₂ (I–Cu, Ag; III–Al, In, Ga; VI–S, Se, Te) ternary semiconductors have potential applications in PEC devices and solar cells because their energy band gaps lie between 1.4 and 2.3 eV. Teuji et al. [3–5] presented visible-light active I–III–VI₂/ZnS solid solution semiconductors controlled by changing in their composition with hydrogen evolution up to 8.2 L/h m² using an aqueous solution containing reagents SO₃²⁻ and S²⁻ under visible-light irradiation. Other In-rich ternary I–III–VI semiconductors with the general formula I–III₅–VI₈ are also interesting photocatalyst materials because of their electrical, optical, and energy properties. The conductivity of I–III₅–VI₈ is usually n-type. The theoretical and practical results show high cell efficiency for the utilization of junctions between p–I–III–VI₂ and n–I–III₅–VI₈ thin films. Efficiencies of the p–CuInS₂/Cu/n–CuIn₅S₈ tandem structure solar cell of 9.1% have been reported in the literature [6]. Chen and Ye [7] also synthesized the visible-light active AgIn₅S₈ powder photocatalyst using the co-precipitation method with a hydrogen evolution rate up to 180 μmol/h-g in an aqueous solution containing reagents

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Table 1The deposition parameters of chemically synthesized p-type AgIn₅S₈ films.

Samples	0.4 M AgNO ₃ (mL)	0.32 M In(NO ₃) ₃ (mL)	0.4 M NH ₄ NO ₃ (mL)	7.4 M TEA (mL)	SbCl ₃ (g)	18 M H ₂ SO ₄ (mL)	0.4 M TAA (mL)	Mole ratios of Ag:In:S:Sb	Dipping numbers
(a)	1.40	1.40	0.70	0.70	0.038	1.40	14.00	1:0.8:10:0.3	3
(b)	1.39	1.39	0.69	0.69	0.051	1.39	13.90	1:0.8:10:0.4	3
(c)	1.38	1.38	0.69	0.69	0.063	1.38	13.80	1:0.8:10:0.5	3
(d)	1.40	1.40	0.70	0.70	0.038	1.40	14.00	1:0.8:10:0.3	4
(e)	1.39	1.39	0.69	0.69	0.051	1.39	13.90	1:0.8:10:0.4	4
(f)	1.38	1.38	0.69	0.69	0.063	1.38	13.80	1:0.8:10:0.5	4

SO₃²⁻ and S²⁻ ions. Although a photocatalyst in powder form is a simple, cheap process to produce hydrogen by irradiation with sunlight, the separation of hydrogen and oxygen decomposed from water and the recycling of these photocatalyst particles consume some energy produced from water splitting. Moreover, for PEC reactions in aqueous electrolytes, p-type semiconductors generally offer more protection against photocorrosion because the semiconductor is cathodically protected under illumination [8]. From the viewpoint of industrial applications, a stable, efficient light absorbing p-type semiconductor thin film reactor is more convenient for collecting hydrogen in a PEC system without any further separation procedure. In order to design an efficient thin film photo reactor, it is necessary to synthesize and study the PEC performance of these new p-type I–III–VI semiconductor films.

The energy band gaps of Ag–In–S ternary semiconductors are located in the range of 1.7–1.9 eV, which can absorb wavelengths of light up to 730 nm. Ag–In–S ternary system semiconductors can be good photo-absorbers in PEC devices and solar cells. Cheng et al. [9,10] presented the synthesis of n-type AgIn₅S₈ film electrodes using chemical bath deposition with a photocurrent density of 6.0 mA/cm² in an aqueous solution containing reagents SO₃²⁻ and S²⁻ ions with an external bias of 3.5 V and a light intensity of 100 mW/cm². Qasrawi [11,12] prepared n-type AgIn₅S₈ films using vacuum evaporation. Yashino et al. [13] prepared Sb-doped AgInS₂ crystals using the hot press method at 400–700 °C and 10 MPa. Albor-Aguilera et al. [14] prepared Sn-doped p-type AgInS₂ films using chemical spray pyrolysis. However, there have been few reports about the synthesis and characterization of p-type AgIn₅S₈ ternary system semiconductor films for PEC applications. In this study, Sb-doped p-type AgIn₅S₈ film electrodes on indium–tin–oxide (ITO) coated glass substrates were synthesized in an aqueous acidic solution using chemical bath deposition. The structural, optical, and PEC responses of the samples were also investigated.

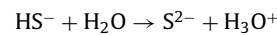
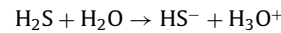
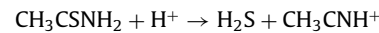
2. Experimental details

2.1. Preparation of p-type AgIn₅S₈ films

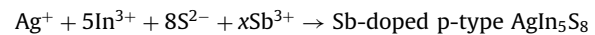
p-type AgIn₅S₈ semiconductor films were deposited on ITO coated glass substrates using chemical bath deposition. ITO coated glass substrates (Union Chemical Co.) were cut into slides (~1 cm × 5 cm) and carefully cleaned ultrasonically in acetone, deionized water, and then ethanol for 30 min. The substrates were then washed carefully in deionized water and dried under ultra-pure nitrogen gas. Silver nitrate (AgNO₃), indium nitrate (In(NO₃)₃ · 5H₂O), thioacetamide (CH₃CSNH₂, TAA), and antimony chloride (SbCl₃) purchased from Merck and Sigma-Aldrich Co. with purity over than 99% were the precursors of Ag⁺, In³⁺, S²⁻, and Sb³⁺, respectively. Triethanolamine (C₆H₁₅NO₃, TEA) and ammonium nitrate (NH₄NO₃) provided from Merck and

Sigma-Aldrich Co. were the sources of the complexing agent and buffer solution, respectively. AgNO₃ of 0.4 M and In(NO₃)₃ of 0.32 M with appropriate volumes were mixed well to obtain the molar ratio of Ag:In as 1:0.8. Triethanolamine of 7.4 M and ammonium nitrate of 0.4 M solutions with appropriate volumes were mixed with reaction solutions containing Ag⁺ and In³⁺ to form the silver and indium complexes solution. In order to avoid the formation of hydroxide-complexes such as In(OH)₃, sulfuric acid was used to keep the pH value of the solution acidic. Thioacetamide of 0.4 M and antimony chloride with appropriate amounts were added into the solution containing silver and indium complexes and mixed well. The final reaction solutions were kept at 20 ml by adding some water into the solution. The detailed deposition parameters are shown in Table 1.

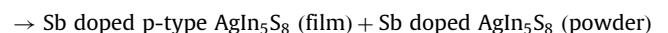
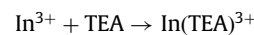
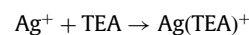
The possible reaction mechanisms of p-type AgIn₅S₈ ternary semiconductor films are:



The cations react with S²⁻ to form Sb-doped p-type AgIn₅S₈ materials.



Most Sb-doped AgIn₅S₈ formed as a powder suspended in the solution instead of as film grown on ITO coated glass substrates because of the low solubility of AgIn₅S₈ in water. In order to minimize the amounts of powders formed, it is necessary to add complexing agents to the solution to form metal complex ions. The most widely used complexing agents are ammonia, triethanolamine (TEA), and sodium citrate. In this study, triethanolamine was used as the complexing agent to control the release rate of Ag⁺ and In³⁺ in the solution. Cations of Ag⁺ and In³⁺ in the solution can be made into complexes by the addition of triethanolamine:



The substrates were placed vertically into a baker containing a freshly prepared aqueous solution with the temperature kept at 80 °C in a thermostat bath. Multiple depositions were carried out with a freshly prepared solution bath for a period of 30 min. After the depositions, the as-deposited films were washed with deionized water in an ultrasonic bath for 5 min and then heat treated at 120 °C in an oven for 60 min. Finally, the films were annealed for 1 h in an evacuated quartz tube at 550 °C for 1 h.

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